Zeolitization characteristics of fly ash and its use to manufacture porous materials

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ABSTRACT

Purpose: At thermal power plants the fly ash (FA) is stored either through dry or wet disposal systems. These storage practices result in different features for fly ashes, such as their interaction with alkalis and hence the potential of zeolite synthesis will be different. With the aim to demonstrate this, it was conducted some investigations to study the physical, chemical, morphological and mineralogical characteristics of the fly ash residues, then were used to synthesis zeolites by a double stage fusion-hydrothermal method.

Design/methodology/approach: The raw and converted fly ash samples were characterized with respect to their composition, crystallinity and morphology, by SEM and XRD analysis. The effects of environment conditions and process parameters on the zeolitization process were studied and analysed.

Findings: The analysis of these residues showed that dry ash attains a high cation exchange capacity (CEC) and SiO_2/Al_2O_3 ratios, which is in agreement to the formation of fly ash zeolites as compared to its counterpart. The experimental results indicate that the fusion temperature does not influence on the synthesis mechanism in range of 500-800 (°C) having only an effect of acceleration. The increasing of alkaline activator/fly ash ratio enhances the zeolitization degree.

Research limitations/implications: The scientific basis for the issues on the zeolitization characteristics of fly ash and its use to manufacture porous materials calls yet for further elucidation and development.

Practical implications: This study helps to establish the superiority of dry ash over wet ash for synthesizing porous materials and their enhanced quantity and quality.

Originality/value: A new route for the fly ash use is demonstrated and this can become an unavoidable task for porous material manufacturing, a viable way to manage this industrial waste and to protect the environment.

Keywords: Dry and wet fly ash, Fusion and hydrothermal synthesis, Fly ash zeolite, Porous material, Industrial waste reuse

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Fly ash (FA) is a fine, glass-like powder recovered from gases resulted by coal-fired in power plant for energy generation [1-3]. Fly ash material particles are solidified while suspended in the exhaust gases and are collected by filter bags or electrostatic precipitators. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape and the size is range from 0.5 μm to 100 μm. They consist mostly of oxides such as silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3). Fly ash is produced in huge quantities in coal-fired energy utility power plants. In the world, the annual volume of fly ash produced by such power plants is reported to be of millions of tons and of this total only 25-30% it has been reported is reused commercially and the difference of 70-75% is disposed of in landfills [1,2]. The disposal of fly ash is one of serious environmental and ecological pollution risk because of the infiltration and leaching of accumulating toxic compounds and elements into soil and the undesirable pH value [2]. More important efforts have been undertaken recently to recycle this industrial [2,3]. For example, about 15-20% of fly ash generated is being used in concrete production. Other uses include road base construction, soil amendment, use as a filler in polymers [1-3]. However, these applications are not sufficient for the complete utilization of the fly ash generated [4-6]. Moreover, the fly ash amount with high concentration in unburned carbon has risen rapidly over the last few years, due to the implementation of increasingly Clean Air Act Regulations regarding NOx emissions [4-7]. The installation of low NOx burners, changes the temperature profile of the flame as well as the flame chemistry. Thus, a hot oxygen rich flame is replaced by a cooler and longer, fuel rich flame. These modifications have proven effective in reducing NOx emissions, but they have also resulted in a lower combustion efficiency, leading to an increase in the amount of unburned carbon in the fly ash. The increasing concentration of unburned carbon, known as (LOI) loss-on ignition, in fly ash has limited the mainly use of ash in the cement industry [7]. This is usually linked to the tendency of unburned carbon to adsorb air-entrainment agents that are added to the cement to prevent crack appearance and their propagation. Fly ashes with LOI higher than 6% are generally unsuitable for the cement industry and consequently, the carbon-rich ash is landfilled. However, this landfill practice results in increasing costs for the utility systems in addition to the loss of revenue from ash sales. In this regard, many researchers have tried to developed new techniques to produce porous materials from unburnt carbon and oxidic fractions contained in fly ash, as substitutes for comercial activated carbon and zeolite materials [4-8]. This is a very important advantage because the fly ash by-product is regarded as a pollutant due to its negative impact on the environment, even if it has alternate, viable and safe uses [9 -14]. The present study tries to demonstrate how to convert the oxide fraction from fly ash into porous materials such as zeolites.

2. Classification and fly ash features

2.1. Classification of the fly ash

There are two grades of fly ash, according to IS 3812:1981 standard as follows: grade I fly ash, which are derived from bituminous coal having fractions $SiO_2+Al_2O_3+Fe_2O_3 > 70\%$ and grade II fly ash, which are derived from lignite coal having fractions $SiO_2+Al_2O_3+Fe_2O_3 >$ greater than 50% [10-17]. On the other hand, ASTM C618 standard specified two categories of fly ash, Class C and Class F depending on the type of coal and the chemical composition (Fig. 1) [18-22]. Class C fly ash, normally is produced from the combustion of lignite or sub bituminous coals, contains calcium oxide (CaO) higher than 10%, with cementitious properties in addition to pozzolanic properties. Class F fly ash, normally is produced from the combustion of bituminous or an anthracite coal, contains calcium oxide (CaO) below 10% and possesses pozzolanic properties. Other classification is based on the boiler operations and is classified with two categories: low temperature(LT) fly ash, that is generated out of combustion temperature below 900°C and high temperature (HT) fly ash, generated out of combustion temperature below 1000°C.

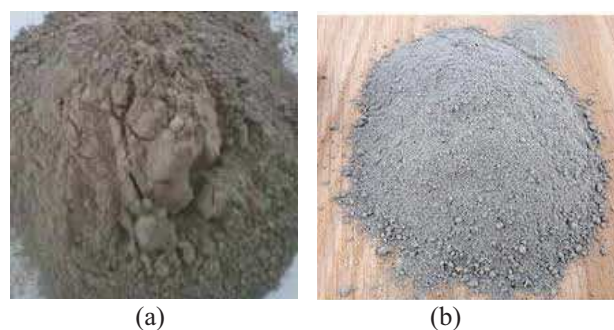(a)   (b)

Fig. 1. Samples of fly ash : (a) Class C; (b) Class F

This limit temperature demarcates the development, in the case of LT, of metakaolinite phases and in the case of

HT fly ash, the same constituents form as reactive glassy phases [23-27]. LT fly ash is preferred for precast building materials such as bricks or blocks. However, so was indicated, the higher ignition loss, of the order of 4-8 percent makes the fly ash less desirable for cement and concrete applications. In contrast, the initial pozzolanic reaction is slow in HT fly ash, which is accelerated with age and this characteristic together with a relatively low ignition loss makes HT fly ash much more suitable raw material for use in cement and concrete industries [28-30].

2.2. Fly ash features

Fly ash is a fine granular material consisting mostly of glassy, spherical particles and some fly ashes also containing angular or irregular particles. Fly ash consists of particles which are generally spherical, typically ranging in size from 10 to 100 μm. Figure 2 shows the scanning electron microscope (SEM) micrographs of bituminous of fly ash particles.
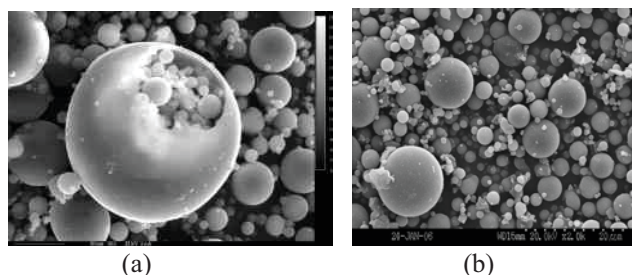

(a)   (b)

Fig. 2. SEM images of coal fly ash: (a) Class C; (b) Class F

Some of these particles appear to be solid, whereas other larger particles appear to be portions of thin, hollow spheres containing many smaller particles. Fly ash can vary in colour from tan to dark gray, this depending on its chemical and mineral components. Tan and light colours are usually associated with a high lime content, while a brow colour is typically associated with the important iron content. A dark gray to black colour is attributed to a higher unburned content. Fly ash colour is usually very specific for each power plant and coal source (Fig. 1).

Dry and wet sieving are commonly used to measure the fineness of fly ashes. ASTM designation C311-77 recommends determining the amount of the sample retained after it is wet sieve done on a 45 μm sieve, in accordance with ASTM method C 430, except that a representative sample of the fly ash is substituted for hydraulic cement in the determination of high calcium fly ashes were finer than low calcium fly ashes. The specific surface of fly ash, which is the area of a unit of mass, can be measured by various techniques. ASTM C204 describes a method for measurement of the surface area and this is in the range 300-500 m^2/kg). Fly ash has a light texture. The reactivity of fly ashes increase with fineness, particularly the fraction passing 45 μm sieve and fineness can be different for dry and wet fly ashes. The specific gravity of different fly ashes varies over a wide range. The specific gravity ranged from a value of 1.90 for a sub-bituminous coal ash to a high value of 2.96 for an iron rich bituminous coal ash. Some sub-bituminous ash had a comparatively low specific gravity of ≈ 2.0, and this shows that hollow particles, such as cenospheres or plerospheres, are present in significant fractions in the ashes. The physical characteristics, in general, of fly ashes vary over a wide range, depending of their source. Fineness is probably influenced more by factors such as coal combustion and ash collection and classification than by the nature of the coal itself. Similarly, the type of fly ash showed no apparent influence on the specific surface as measured by the Blaine technique. Moreover, except in some cases, there was very little relationship between the specific surface as measured by the Blaine and the fineness as determined by percentage retained on a 45μm sieve. The pH values vary from 1.2 to 12.5, with most ashes tending toward alkalinity [17,18]. The pH value of the ash-water system depends mainly on the Ca/S molar ratio in ash, although other minor alkalis or alkaline earth cations may also contribute to the balance [22,23]. Based on the Ca/S ratio and pH value, fly ash can be classified into three main groups: acidic ash (pH < 7), mildly alkaline ash (pH 8-9), and strongly alkaline ash (pH 11-13).

The chemical composition of fly ash depends on the sources of coal and also on operating parameters of system, thus the quality various from source to source and within the source also. With use of pulverized coal and efficient combustion system, LOI (Loss on ignition) is a measurement of unburned carbon remaining in the ash. Variation in LOI can contribute to fluctuations in air content and call for more careful field monitoring of entrained air in the concrete.

The irregular fragments from fly ash consist mainly of unburnt carbon, calcite and anhydrate. Coal fly ash is one of the most complex materials that can be analyzed and characterized. Approximately 188 mineral groups and 316 individual minerals have been determined in different ash samples [2,3] major compounds are metallic oxides and varying contents of unburnt carbon as determined by a loss on ignition (LOI) test.

The contents of main oxides are usually in a such order: $SiO_2 > Al_2O_3 > Fe_2O_3 > CaO > MgO > K_2O > Na_2O$. Fly ash also contains much more trace elements, some of which are

of environmental hazard. Elements such as As, Al, Cu, Cr, Pb, Ni, Ba, Sr, Hg, V and Zn are present in significant quantities. Because of this, mobility and leaching studies have been achieved to assess the probability of these elements migrating to the environment [19,26].

2.3. Environmental hazards of fly ash

The impact on environment of coal fly ash has been totally recognized. The most ash disposal methods lead to the dumping of huge quantity of fly ash on open land. In many countries, coal fly ash is considered as a solid waste and its treatment is not subject to regulation as a hazardous waste. Irregular accumulation of fly ash and its inappropriate disposal leads to disposal over large areas of land, with a resultant of soil degradation and danger to both people health and the environment. A lot of part of fly ash particles are small enough to escape emission control devices and they are easily suspended in air and have become a major source of atmosphere pollution. Repeated exposure to fly ash small particles can cause irritation of the eyes, skin, nose, throat and respiratory tract, and can even result in poisoning with arsenic or other trace toxic elements. Fly ash can even reach the sub-soil and cause clog natural drainage systems and finally to contaminate the ground water with heavy toxic metals. Coal contains a significant amount of different trace metals, and after coal combustion these metal concentrations are sometimes 4-10 times higher in fly ash than that of in parent coal. Coal fly ash can be regarded as a major potential source of releasing many environmentally pollutant elements to the environment. Factors, such as initial concentration of trace elements, the particle size, pH value of extraction solution, solid/liquid ratio and leaching time influence the mobility of the trace elements in aqueous environments [6].Under favouring conditions, a considerable amount of trace elements from surface fly ash particles can easily be leached out by the their interaction with water in landfills [20]. These water-soluble trace elements contaminate the surface and ground water and soil [7,31].

3. Experimental part

3.1. Fractions separation from fly ash samples

Samples with high unburned carbon content, titled dry fly ash (DFA/FA01) and wet fly ash (WFA/FA02) were provided from thermal power plants from local area, and these were characterized to determine their physical and chemical properties. DFA sample was generated from the combustion of pit coal in a pulverized boiler equipped with a low-NOx burner. The WFA sample was taken from a gasifier that uses a lower coal as fuel such as peat. These samples were chosen because they contain a big amount of unburned carbon, so high loss- on- ignition (LOI) value (Table 1). DFA and WFA samples represent the average of 12 samples for each, collected during three months (April-June 2016).

Table 1.
Chemical composition of the initial dry and wet fly ash samples (DFA and WFA respectively)

Oxide	(wt.%)	
	DFA	WFA
SiO_2	63.82	58.31
Al_2O_3	26.04	27.05
Fe_2O_3	5.12	5.03
$SiO_2 + Al_2O_3 + Fe_2O_3$	94.98	90.39
CaO	1.92	1.16
MgO	0.38	0.52
Na_2O	0.08	0.21
K_2O	0.67	0.89
TiO_2	1.53	1.61
P_2O_5	0.15	0.27

Values represent the average of 12 samples for each

The fly ash samples were sieved into (+140) mesh and (−140) mesh fractions. The fraction of (+140) mesh fraction was used to prepare carbon sorbents because previous researches have shown that most of the unburned carbon is found in fly ash particles of size ≥ 100 µm (which corresponds to + 140 mesh) [4,6]. The fly ash fraction of (−140) mesh was used to prepare zeolite porous material. Fly ash composition (oxides) was determined by X-ray fluorescence (XRF) spectrometry using a spectrometer Philips PW1606.The proximate and ultimate analysis was made using a FLASH-2000 Elemental Analyzer. All chemicals used in the investigations were of analytical grade. The morphology of samples was examined by scanning electronic microscopy (SEM) using Jeol JSM-7000 microscope equipped with an energy dispersive detector (EDS).Loss-on- ignition (LOI) value of the samples was determined according to the ASTM C311 standard.

A quantity of 3000 g (+140 mesh) of fly ash sample (DFA/WFA) was dispersed in 6 litres of water and stirring to wet the sample and then a plunger type magnet was used to recover magnetic components. The unburnt carbon fraction was collected was collected from the surface of the flotation bath, while the oxide fraction was collected from the bottom of the flotation bath. The resulting concentrate was dried overnight and then weighted in order to

determine the quantity of the obtained sample. Further the unburned carbon and oxidic fractions separated from fly ash samples were processing in a two step procedure involving ball milling and sieving through a 170 mesh screen. For milling it was used a Fritsch planetary ball mill with stainless steels balls and vials. Balls to fly ash mass ratio corresponded to 20:1, milling time was set 20 min and was sufficient to obtain unburned carbon and oxidic fly ash particles size $\leq$ 90 μm (–170 mesh). The –170 mesh particles were cleaned by froth flotation technique according to procedure presented in reference [27].

3.2. Hydrothermal treatment

NaOH in pellets form was supplied by Thomas Baker Ltd., and were dissolved in the distilled water for the preparation of solutions of different concentration (0.5; 1.0; 2.0, 3.0 and 3.5 M). To ensure the interaction of alkali-oxidic ash fraction, the liquid-to-solid ratio (L/S), (slurry of oxidic fly ash and the NaOH solution) was maintained at 10:1 (ml/g) [6]. This mixed slurry was heated in an open reflux system at 100°C for different times (T = 8 to 48 hours, with an increment of 8 hours). The residues from this hydrothermal treatment designated as DFAR and WFAR (i.e., alkali activated dry ash and alkali activated wet ash, respectively) were characterized for their characteristics (specific gravity, cation-exchange capacity, mineralogy and morphology, chemical composition). Details on the methodology used for this purpose are presented below. For the sake of clarity, the DFAR and WFAR samples are designated as described below:

DFARxy where x represents the concentration of alkaline solution (range 0.5-3.5 M) and y represents time period (range 8-48 hours).

3.3. Characteristics determination

The specific gravity, G, was determined with the Helium gas Ultra Pycnometer (Quantachrome, USA), using ASTM D 5550 [22]. This instrument measures the volume of helium gas displaced from the sample chamber for a known weight of the samples. Using this volume (which is equal to the volume of the sample) the specific gravity (the density with respect to water) of the sample was determined. Fly ash composition (oxides) was determined by X-ray fluorescence (XRF) spectrometry using a spectrometer Philips PW1606.The proximate and ultimate analysis was made using a FLASH-2000 Elemental Analyzer. All chemicals used in the investigations were of analytical grade. The morphology of samples was examined by scanning electronic microscopy (SEM) using

Jeol JSM-7000 microscope equipped with an energy dispersive detector (EDS).Loss-on-ignition (LOI) value of the samples was determined according to the ASTM C311 standard. The cation-exchange capacity, CEC, of the ash samples were determined by adopting the methodology presented in ASTM D7503-10.

4. Results and discussion

4.1. Separation efficiency of fly ash fractions

The use of fly ash as a raw material for the manufacture of porous material requires an initial step of separating the component fractions, namely the unburned carbon fraction, which can be used to produce carbonaceous porous material and the oxide fraction that can be used for the production of zeolites. Certain fly ash with a high content in unburned carbon are a mixture between oxides and carbon and is characterized by a bi-modal particle size distribution in which the particle size of unburned carbon is biased toward the coarse size fractions of the mixture, while the particle size of the oxides component of the fly ash is biased toward the fine size fraction of the mixture. In such mixtures, the weight fraction of the unburned carbon component generally decreases and the weight oxide fraction of the fly ash component in the mixture increases in an exponential fashion as the particle size component of the fly ash decreases. Oxide fraction/unburned carbon fraction mixtures from fly ash exhibiting such bimodal particle size distribution, called abbreviated "bi-modal fly ash" normally are characterized by particle size distribution curves for each component similar to those illustrated in Figure 3, with the arrows adjacent the words "coarse" and "fine" indicating the direction of increasing in each characteristic.
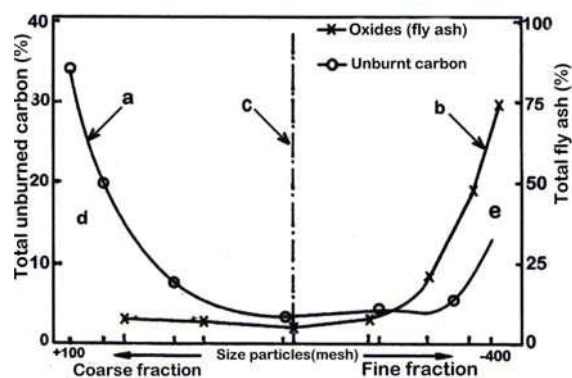

Fig. 3. Curves for particle size distribution of oxide fraction and unburned carbon fraction in fly ash

Based on this distribution, the fly ash samples examined in the experiments performed were separated into the component fractions (Fig. 4).
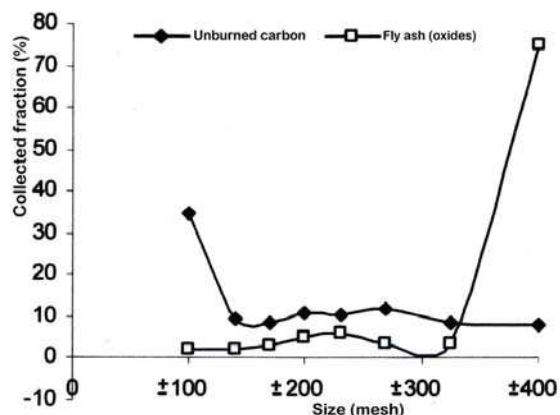

Fig. 4. Curves for particle size distribution of oxide fraction and unburned carbon fraction in dry fly ash sample (DFA)

The examples illustrate that satisfactory carbon removal from bi-modal fly ash can be achieved by subjecting bi-modal fly ash to separation process. The total cumulative weight distributions of the carbon component and oxide fly ash component of the bi-modal dry fly ash sample (DFA) prior treatment is shown in Figure 3.

Using sieving and froth flotation separation techniques the fractions from dry and wet fly ash samples were separated. In Figure 5 is presented the separation efficiency in magnetic, unburned carbon and clean ash fractions using sieving and froth flotation separation techniques.
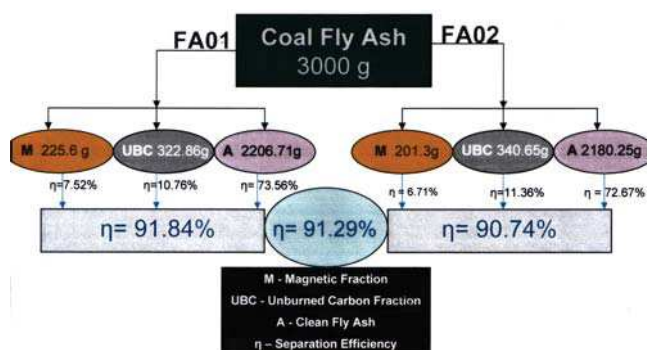

Fig. 5.Separation efficiency in magnetic, unburned carbon and clean ash fractions using sieving and froth flotation separation techniques

From experimental data it could determine that if the initial sample has a weight of 3000 g, the magnetic concentrate has represented 225.6 g in case of DFA sample and 201.3 g for WFA sample, while the unburned carbon fraction was 322.86 g for DFA sample and 340.65 g for WFA sample respectively. The obtained clean fly ash fraction was 2206.71 g for DFA sample and 2180.25 g for WFA sample respectively. For both tested samples the efficiency of the separation process in the three fractions (magnetic concentrate, unburned carbon and clean fly ash) was greater than 90% (91.84% to 90.74% for DFA sample and WFA sample, respectively). The unburned carbon in fly ash was concentrated from about 11 wt.% to about 70 wt.%. It can conclude that sieving and froth flotation are suitable techniques to separate the component fraction from fly ash samples, this conclusion being underlined and in other studies [11,12].

4.2. Specific gravity, chemical composition and Si/Al ratio determination

From determined data it is clear that the specific gravity, G, of dry fly ash (DFA), (= 2.17) is almost same as that of wet fly ash (WFA), (= 2.12). Though, in general, G values for the WFA and DFA samples are seen to increase with an increase in the concentration of the NaOH (M≤2.0), randomness in the value of G for the DFA with time (T) is noticeable. Incidentally, the residues $DFA_{(1,36)}$ (i.e., the dry fly ash treated with 1 M NaOH solution for 36 hours) and wet fly ash WFA(1,24) (i.e., $WFA_{(1,24)}$ sample treated with 1 M NaOH solution for 24 hours), exhibit very high G values (2.71 and 2.52, respectively). The increase in G value can be attributed to the etching of the ash particles, which helps in the escape of entrapped air and gases from the inner regions of the fly ash particles, due to an alkali treatment [6,7]. On the other hand, treatment of the fly ash with high molar solutions (i.e., M≥2.0), results in a significant increment (up to 2.65) and reduction (up to 2.32) in the G values of the WFA and DFA samples, respectively. This could be attributed to a gradual increasing in the dissolution of the lighter components (e.g., cenospheres) present in the wet ash sample, as compared to the dry ash sample, for which the reaction is faster, even at lower alkali concentration (Fig. 6). Also, as is shown in Figure 6a, the DFA samples develop much more internal pores, which supports the increased zeolite formation process and results in lower G values. The increased zeolite formation in DFA samples is also justified by the important dissolution of SiO_2 (e.g., from 63.81%, for the DFA, to 36.93%, for WFA, which is 26%) and Al_2O_3 (from 26.03%, to 18.72%, which is 6.9%). This dissolution of SiO_2 and Al_2O_3 also results in enhanced pores on the residue particles (see micrographs of the residues in Fig. 6).
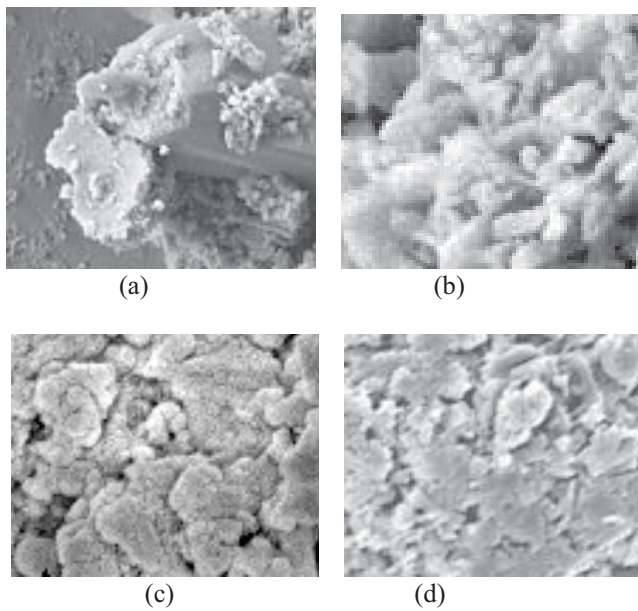
(a) (b)

(c) (d)

Fig. 6. SEM micrographs of the residue samples (a) $DFA_{(1,24)}$ x 6000; (b) $DFA_{(1,24)}$ x 30000; (c) $DFA_{(3.5,36)}$ x 50000; (d) $DFA_{(3.5,12)}$ x 25000

Table 1 shows the chemical composition of the initial dry and wet fly ash samples. Also the content of SiO_2 and Al_2O_3 and their ratio designated as (Si/Al) R are shown in Tables 2 and 3.

Table 2.
Silicium and aluminium oxides and their ratio in the dry fly ash samples

Fly ash	Residue	SiO_2 (wt.%)	Al_2O_3	(Si/Al)R
	$DFA_{0,0\ (initial)}$	63.82	26.04	2.45
	$DFA_{0.5,8}$	57.72	27.91	2.06
	$DFA_{0.5,16}$	55.68	25.27	2.20
	$DFA_{0.5,24}$	54.75	21.72	2.52
	$DFA_{0.5,32}$	54.71	21.68	2.51
	$DFA_{0.5,40}$	50.68	20.26	2.50
	$DFA_{0.5,48}$	48.62	18.38	2.64
	$DFA_{1,8}$	47.18	18.01	2.61
	$DFA_{1,16}$	46.64	17.95	2.59
	$DFA_{1,24}$	46.12	17.56	2.62
	$DFA_{1,32}$	44.57	18.02	2.47
	$DFA_{1,40}$	44.06	18.21	2.41
	$DFA_{1,48}$	45.52	17.93	2.53
DFA	$DFA_{2,8}$	41.82	18.41	2.27
	$DFA_{2,16}$	42.21	20.03	2.11
	$DFA_{2,24}$	38.64	26.02	1.48
	$DFA_{2,32}$	39.52	19.05	2.07
	$DFA_{2,40}$	43.06	19.41	2.21
	$DFA_{2,48}$	51.42	23.66	2.17
	$DFA_{3,8}$	50.12	21.68	2.31
	$DFA_{3,16}$	48.47	19.68	2.46
	$DFA_{3,24}$	45.21	18.04	2.50
	$DFA_{3,32}$	44.87	17.94	2.50
	$DFA_{3,\ 40}$	43.54	18.05	2.41
	$DFA_{3,48}$	41.68	17.76	2.34
	$DFA_{3.5,8}$	41.03	18.04	2.27
	$DFA_{3.5,16}$	39.85	17.68	2.25
	$DFA_{3.5,24}$	35.46	19.70	1.80
	$DFA_{3.5,32}$	35.23	17.07	2.06
	$DFA_{3.5,40}$	30.34	16.31	1.86
	$DFA_{3.5,48}$	28.26	14.31	1.97

DFA_{xy} (where x represents the concentration of alkaline solution – range 0.5-3.5 M, and y represents time period – range 8-48 hours)

Table 3.
Silicium and aluminium oxides and their ratio in the wet ly ash samples

Fly ash	Residue	SiO$_2$	Al$_2$O$_3$	(Si/Al)R
		(wt.%)		
	WFA$_{0,0(initial)}$	58.31	27.05	2.15
	WFA$_{0.5,8}$	64.06	28.01	2.28
	WFA$_{0.5,16}$	63.24	31.07	2.03
	WFA$_{0.5,24}$	62.19	29.13	2.13
	WFA$_{0.5,32}$	59.43	29.03	2.04
	WFA$_{0.5,40}$	62.14	31.03	2.01
	WFA$_{0.5,48}$	58.54	30.02	1.95
	WFA$_{1,8}$	59.04	30.32	1.94
	WFA$_{1,16}$	59.17	30.83	1.91
	WFA$_{1,24}$	58.84	31.21	1.98
	WFA$_{1,32}$	59.65	30.89	1.93
	WFA$_{1,40}$	58.91	31.06	1.89
	WFA$_{1,48}$	57.05	30.72	1.85
WFA	WFA$_{2,8}$	57.11	30.03	1.90
	WFA$_{2,16}$	57.01	30.13	1.89
	WFA$_{2,24}$	56.94	32.26	1.76
	WFA$_{2,32}$	56.41	31.85	1.77
	WFA$_{2,40}$	55.52	30.95	1.79
	WFA$_{2,48}$	53.88	34.08	1.87
	WFA$_{3,8}$	54.14	31.05	1.74
	WFA$_{3,16}$	55.07	31.65	1.74
	WFA$_{3,24}$	54.65	31.86	1.73
	WFA$_{3,32}$	54.03	30.94	1.75
	WFA$_{3,40}$	53.87	30.56	1.76
	WFA$_{3,48}$	52.86	30.78	1.77
	WFA$_{3.5,8}$	51.93	31.15	1.67
	WFA$_{3.5,16}$	49.96	30.85	1.62
	WFA$_{3.5,24}$	43.28	32.25	1.34
	WFA$_{3.5,32}$	42.79	32.18	1.33
	WFA$_{3.5,40}$	40.88	32.05	1.27
	WFA$_{3.5,48}$	40.57	32.38	1.25

WFA$_{xy}$ (where x represents the concentration of alkaline solution – range 0.5-3.5 M, and y represents time period – range 8-48 hours)

From Tables 2 and 3 it can be seen that though both DFA and WFA fly ash belong to class F [23], as SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ is more than 70%, the content of SiO$_2$ in the DFA is higher than 5.51%, as compared to the WFA.

This amount of SiO$_2$ in excess in the DFA could be in the amorphous aluminosilicate glass phase, this being responsible for a higher silica dissolution, as shown in Table 2. Such a reduced (Si/Al)R (lower than 2.45 in the DFA) can be attributed to either a loss of SiO$_2$ or an advantage of Al$_2$O$_3$ in these residues. This also indicates mineralogical and morphological transitions, which further enforces the probability of zeolitization of the DFA. In contrast, Table 3 exhibits an increase in SiO$_2$ in some of the residues.

Also, Al$_2$O$_3$ has been noticed to be on the higher side, as compared to the WFA. However, such an increase in the oxides in the residues of WFA was unexpected and could not be substantiated, as neither SiO$_2$ nor Al$_2$O$_3$ were added externally and an extensive study is required to explore and explain the chemistry involved in this entire process.

4.3. Correlation between Si/Al ratio and CEC

Furthermore, it can be inferred that the increasing in Al$_2$O$_3$ in the WFA samples contributes to a significant lowering of their (Si/Al)R up to 1.25 (Table 3). Also, a decreasing in the (Si/Al)R of the WFA samples with an increase in the molarity of alkali solution (M) and time (T) of the treatment have some effects on their increasing specific gravity (G), as shown by values determined for this characteristic. Thus, based on the (Si/Al)R values, it can be

concluded that the wet ash used in this study is a suitable material for the synthesis of a group of low-silica zeolites (2>(Si/Al)R>1.26), such as Na-P1 and hydroxysodalite. Incidentally, these zeolites have been identified from the XRD diffractograms of the samples, as presented in Table 3. This study also reveals the higher zeolitization potential of the DFA for synthesizing a class of zeolites with a slightly higher (Si/Al)R value (2.64 > (Si/Al)R >1.62), which is responsible for the creation of the zeolites faujasite and analcime [27].

The variation of the cation-exchange capacity (CEC) of the residues with respect to the concentration of NaOH solution molarity, M, is reflected in Figures 7 and 8.
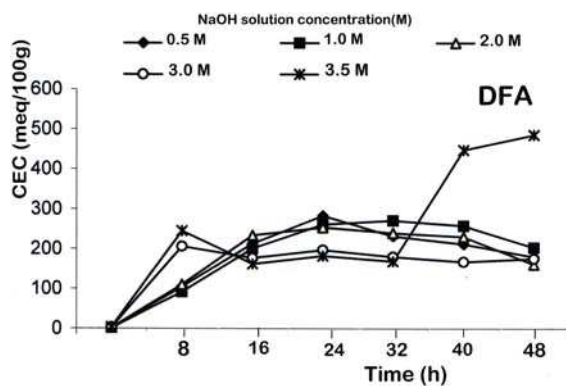

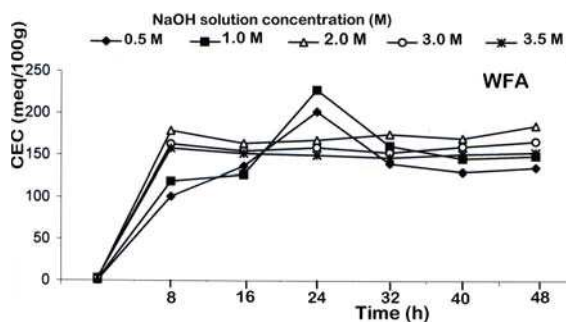Fig. 7. Variation in the CEC of the DFA fly ash samples

Fig. 8. Variation in the CEC of the WFA fly ash samples

It can be observed from Figures 7and 8, that the trends are not very well defined, but the DFA samples exposed a higher CEC than the WFA samples. This characteristic also confirms the higher zeolitization of the DFA samples, as compared to its counterpart (WFA samples). It should also be noted that some of the DFA residues (i.e., DFA0.5,24; DFA3.5,40; DFA3.5,48) exhibit very high CEC values (283, 448,and 486 meq/100g, respectively). Also it was made an attempt to develop a correlation between the CEC and (Si/Al)R of the residues, as presented in Figure 9.
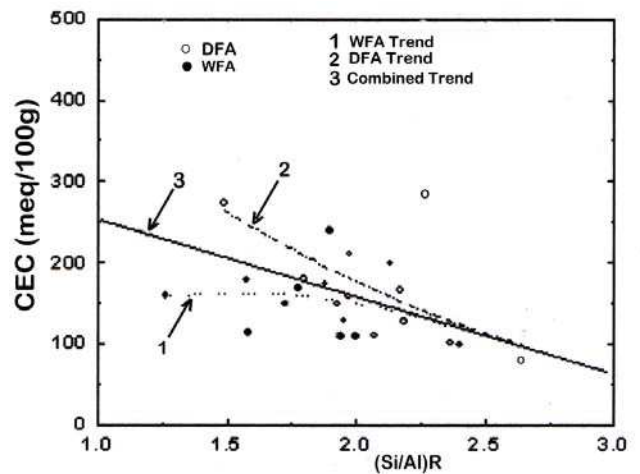

Fig. 9. The correlations between CEC and (Si/Al)R of the DFA and WFA solid residues

It is eloquent that, in general, the CEC decreases with an increasing in (Si/Al)R. However, the rate of this decreasing (defined in terms of the relationship slope) is significantly fast for the DFA, as compared to the WFA. This also showed that the DFA is a much more suitable and active material to synthesize a higher grade of cation exchange material (i.e., a zeolite) than the WFA. A combined trend for the DFA and WFA samples is presented in the Figure 9, which could be very important and useful for predicting the CEC of the activated fly ashes if their (Si/Al)R is determined and known.

4.4. Mineralogical and morphological aspects

In Figures 10 and 11 are showed the SEM micrographs for studied samples.

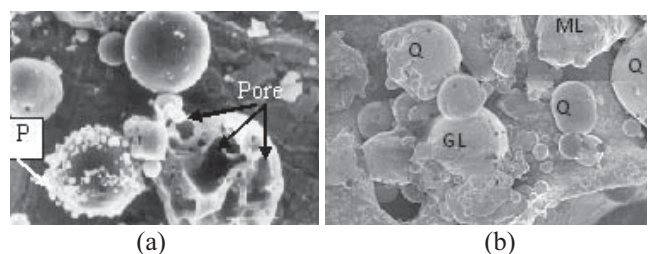(a)   (b)

Fig. 10. SEM micrographs of the residue samples (a) DFA and (b) WFA where Q, GL, ML, P represent quartz, glass, mullite and zeolite-P, respectively

As is presented in Figures 10 and 11 the WFA samples contain zeolite Na-P and in addition the residue WFA exhibits the presence of the zeolite Na-P for M ≤1 [21].

Incidentally, the zeolite hydroxysodalite appears in the residue for solution concentration M≥1. However, the zeolites analcime and cancrinite were also found in the residues. This could be attributed to the dissolution of mullite and hence the enhanced zeolitization of the dry fly ash. Also, newly formed peaks, Figure 12 (2θ° equal to 12.57° and 28.18°) exhibit an increase in the peak intensity with an increase in the molarity of alkali solution (M≤1) and for activation time, T≤24 hours.

_____ 50 μm   _____ 50 μm
      (a)   (b)
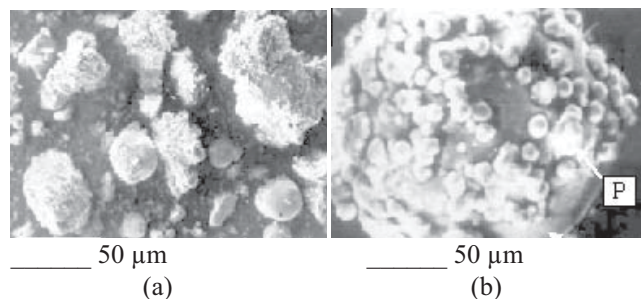
Fig. 11. SEM micrographs of the WFA residue samples WFA$_{(1,24)}$ at different magnifications: (a) x 2500 and (b) x 5000
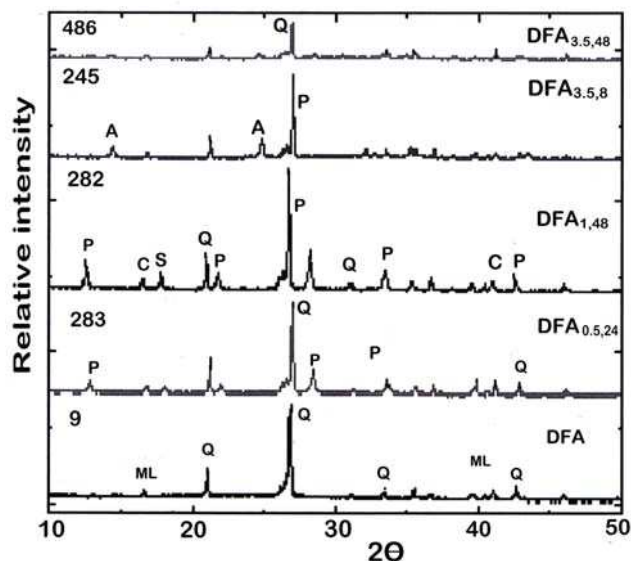

Fig. 12. X-ray diffractogram of initial DFA and DFA residue samples. A,Q, ML, C,P and S represent analcime, quartz, mullite, cancrinite, zeolite Na-P and hydroxisodalite, respectively

It also can be seen that the residues exhibit other two new and small peaks of analcime zeolite. Accidentally, these and other peaks present in residues disappear for

a higher molarity of the alkali concentration and an activation time much longer. As was explained, a high CEC (48 meq/100g) of the residue DFA$_{3.5,48}$, indicates a highly soft grade and also fibrous and porous (Figure 12 – low intensity peaks) of zeolites in the residue. Furthermore, the presence of a little quartz and negligible mullite in the residues reveals the suitability of the dry fly ash for the synthesis of better porous zeolites. From Figure 10a,b it can be observed that both DFA and WFA samples are enriched with oval and spheric particles, which can correspond to quartz and glass respectively. However, Figure 4b exhibits some whitish spheres (zeolite Na-P with big surface pores) deposited on the WFA samples. This is due to the water-ash interaction that take place in the wet fly ash [7,21,28]. In contrast, the micrograph of the DFA (as depicted in Fig. 11b), presents much more smooth and spherical (quartz, mullite) to irregular particles (hematite/ magnetite, carbon) as reported in reference [1] and [5]. It can also be noted that a spherical particle, in DFA$_{1,24}$, has been totally covered by zeolites. The majority of the fibrous and spherical products are zeolite Na-P and hydroxysodalie, respectively [14,16]. Above all, the cluster of whitish orthorhombic products formed in the dry fly ash residue samples confirms the significant zeolitization of the DFA samples. In agreement with the X-ray diffractograms (see Fig. 12), the formation of the zeolite morphology corresponds to the appearance of new mineral peaks and the residue of the DFA (corresponding to 3.5M NaOH and 48 hours of treatment) shows the synthesis of the majority of zeolite Na-P with big inter-particle pores and a high CEC up to 486 meq/100g.

5. Conclusions

By this research it has established the utility of fly ash as a raw material for the synthesis porous materials such as zeolites, referred to as fly ash zeolites (FAZs). However, in general the quality of the fly ash has showed to be dependent on the type of disposal (wet or dry disposal systems) used by the power plants. The hopper systems of the electrostatic precipitators (dry disposal system of the fly ash) do not involve water-ash interaction, while, when fly ash is transformed into a slurry for its storage, (known as wet disposal), such an interaction occurs over a long period. Though this water-ash interaction, known as zeolitization process, has studied and it was explored the influence of the disposal practices used at power plant on the zeolitization characteristics of the fly ash and the types of zeolites formed. It has showed that water-ash interaction results in an alteration of the physical, mineralogical,

morphological and chemical characteristics of the fly ash. Furthermore, this study has highlighted the fact that the type of zeolites resulted at the end of this interaction, their specific gravity, cation-exchange capacity, mineralogical and morphological phases depend on the composition of the fly ash and also of the water-ash interaction conditions. By these factors, the uncertainties are mostly responsible for generating of controversy about the grade and quality of the fly ash zeolites that resulted at the end of the hydrothermal treatment, and the influence of the source of fly ash, from dry or wet disposal systems, on the grade and quality of fly ash zeolites can not be ignored. The majority of the zeolite Na-P can be synthesized from dry ash along with traces of zeolite hydroxysodalite, analcime and cancrinite by the hydrothermal treatment of the ash using 1.0M to 3.5M NaOH solution and 24 to 48 hours of activation time. A combined trend derived between the cation exchange capacity (CEC) and the silica alumina ratio (Si/Al) of an activated fly ash is demonstrated to be very useful for predicting its zeolitization potential. From another point of view, unburned carbon fraction is very similar to the precursors for production of carbon materials, such as selective carbon sorbents. This carbon sorbents obtained from unburned carbon have a significant lower cost and advantage over comercial carbon sorbents. Therefore, separation of unburned carbon fraction from fly ash is beneficial to coal fly ash application, either for carbon recycling or mineral coal fly ash application in cement industry and zeolite synthesis.

Acknowledgements

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